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Graphene nanoplatelets as a multifunctional filler for polymer foams

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Abstract

Due to their high mechanical and transport properties, graphene-derived materials have aroused a great deal of interest in the most varied sectors. Among these, graphene nanoplatelets have been gaining interest due to the fact they can be synthesized in a way scalable to mass production, enabling them to be considered in the preparation of polymer nanocomposites. Nevertheless, the addition of graphene nanoplatelets into polymers using industrial melt-mixing machinery is still a challenge, mainly related to inadequate graphene dispersion during processing. Foaming could come as a possible strategy to maximize the efficiency of graphene nanoplatelets in polymers by improving its dispersion throughout the polymer matrix, at the same time enabling to considerably reduce the material's density. This paper considers experimental examples of the improvement of the specific mechanical properties and enhancement of the electrical conductivity of different types of polymer foams thought for the most varied applications by incorporating graphene nanoplatelets using conventional plastic processing technologies, with the goal of developing new multifunctional lightweight polymer nanocomposites.

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Keywords: Graphene nanoplatelets; polymer foams; multifunctional; electrical conductivity

1. Introduction

Graphene is the name given to a flat monolayer of carbon atoms tightly packed into a honeycomb-like carbon lattice where the sp^2 hybridized carbon atoms are arranged in a regular hexagonal pattern in a 2D layer [1]. Although having been studied for over sixty years and widely used for describing the properties of various carbon-based materials, graphene was believed to be unstable with respect to the formation of curved structures such as fullerenes or nanotubes. Unexpectedly, Geim and Novoselov proved in 2004 that free-standing graphene was possible [2].

Graphene and graphene-derived materials have aroused a great deal of interest because monolayer graphene has been shown to be about 100 times stronger than steel with a theoretical modulus around 1 TPa and strength of 150

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GPa [3], to conduct electricity better than copper in the in-plane direction and to show improved barrier properties due to its platelet-like morphology. Also, owing to its atomic thickness, graphene presents a high specific surface area with high possibility of interaction with other substrates [1]. Nevertheless, as happens with other nanosized graphitic structures, single layer graphene synthesis is still challenging, especially in terms of attaining considerable quantities for industrial implementation. Two main types of graphene-derived materials have been gaining ground in terms of possible large-scale production: reduced graphene oxide (RGO) and graphene nanoplatelets (GnP). RGO may be obtained by the chemical or thermal reduction of graphene oxide (GO), usually synthesized through the oxidation of graphite by means of the Hummers method. Nonetheless, reduction of GO generates structural defects in the carbon lattice, considerably reducing the electrical properties when compared to pristine graphene [1]. GnP, which are unique nanoparticles consisting of short stacks of graphene sheets obtained by the previous intercalation of small molecules between graphite layers and later mechanical/thermal exfoliation [4], have surged as a possible alternative to RGO.

Due to its mass production scalability, one of the most immediate applications of GnP is in the preparation of polymer nanocomposites. Among the possible benefits of adding GnP into polymer systems is mass reduction resulting from low loading, increased stiffness and possible increased toughness, enhanced electrical and thermal conductivities or improved barrier properties, resulting in nanocomposites with multiple enhanced characteristics [5-6]. Nevertheless, the processing of polymer nanocomposites containing GnP is still a challenge, especially when using industrial melt-compounding techniques, mainly related to their low loading concentrations and difficulties in guaranteeing proper nanoplatelet dispersion throughout the polymer matrix. Also, due to their particular chemical nature, carbon-based GnPs tend to aggregate during processing, limiting their possible nanoscale reinforcement effect and the overall mechanical and transport performance of the resulting nanocomposite [5-6].

Foaming has recently been demonstrated to promote the dispersion of nanoparticles such as GnP throughout a given polymer by favoring nanoplatelet separation during expansion, hence coming as a possible strategy to attain maximum nanoparticle efficiency. Interesting synergistic effects result from combining the concept of polymer nanocomposite with that of polymer foam, as on the one hand the addition of GnP may counteract the loss in overall mechanical performance resulting from density reduction and add functional characteristics not commonly found in foams, and, on the other hand, foaming may favor GnP dispersion [7-9]. Additionally, the incorporation of nanoparticles, combined with a proper control of the foaming parameters, could result in microcellular foams, which have been shown under specific conditions to display specific mechanical properties even higher than that of the respective unfoamed base material [10], surpassing the problems related to the very stringent foaming conditions required for their industrial implementation.

This work presents experimental examples of the possible improvements of the mechanical properties and enhancement of the electrical conductivity of different polymer foams, from foams based on commodity plastics to those based on high performance plastics for the most varied applications by incorporating GnP using conventional plastic processing technologies, showing the viable use of GnP as a multifunctional filler for polymer foams.

2. Experimental

2.1. Materials

Three polymer-based formulations have been selected as examples of the effects of GnP addition in the resulting foam properties: a polypropylene (PP)-based formulation, selected as example of a high consumption plastic, polycarbonate (PC), example of a technical plastic, and polyetherimide (PEI) as high performance plastic.

In the case of PP, a PP-based material was specifically formulated for both physical and chemical foaming by melt-compounding 50 parts per hundred (phr) of a high-melt strength PP (HMS-PP) with the commercial name Daploy WB130HMS (Borealis) and 50 phr of a linear PP, Moplen HP 501L (LyondellBasell) with stearic acid (1 phr) and the remaining components. The original HMS-PP has a melt flow index (MFI) of 2.1 dg/min measured at 230 ºC and 2.16 kg according to ISO 1133 and a melt strength and extensibility at break, both measured at 200 ºC, of 34 cN and 220 mm/s, respectively. The linear PP has an MFI of 6.0 dg/min, also determined at 230 ºC and 2.16 kg (ISO 1133). PC, with the commercial name Lexan-123 R, was supplied in the form of pellets by Sabic. Said PC has a density of 1.2 g/cm^3 and an MFI of 17.5 dg/min, measured at 300 ºC and 1.2 kg (ISO 1133). PEI, with the

commercial name Ultem 1000, was provided by Sabic in the form of transparent amber color solid bars. Ultem 1000 has a density of 1.27 g/cm^3 and a glass transition temperature (T_g) of 217 ºC.

Graphene nanoplatelets, with the commercial name xGnP-M-15, were supplied by XG Sciences. This material has a density of 2.2 g/cm^3 and is formed by short stacks of graphene sheets with an approximate thickness of 6-8 nm, i.e., each stack being formed by a number of individual graphene sheets of around 12 to 16, and diameter of 15 μm, a typical surface area of 120-150 m^2/g and an electrical resistivity of 10^7 and 10^2 S/m, respectively measured parallel and perpendicular to its surface, as reported by the manufacturer.

In the case of the chemically-foamed PP, azodicarbonamide (ADC) was added as an additive to the polymer during the melt-compounding stage at a fixed concentration of 1.5 phr. The added ADC was a commercial grade, Porofor ADC/M-C1 (Lanxess Energizing Chemistry), with a density of 1.65 g/cm^3 and particle size of 3.9 ± 0.6 μm.

N-methyl pyrrolidone (NMP), used as solvent in PEI foam preparation, was acquired from Panreac (purity: 99%).

2.2. Foam preparation

PP foams were prepared by both physical and chemical foaming. In the case of physical foaming, PP composites containing 2.5 and 5 wt% GnP, previously prepared by melt-mixing the PP-based formulation with the corresponding amount of GnP, were foamed by supercritical CO_2 (sCO_2) dissolution. In the case of chemical foaming, besides GnP, ADC was incorporated as chemical blowing agent, with foams being obtained by compression-moulding chemical foaming (for details consult [11]). PC composites containing a fixed amount of 0.5 wt% GnP prepared by melt-compounding were foamed by sCO_2 dissolution inside a high pressure vessel applying a high pressure drop (for details consult [12]). In the case of PEI foams, different amounts of GnP were first dispersed in NMP and ultrasonicated. PEI was dissolved in each suspension in order to prepare solutions of PEI with variable amounts of GnP (1, 2, 5 and 10 wt% GnP), which were poured on a flat glass and exposed to air with a controlled humidity, promoting foaming by water vapor-induced phase separation (WVIPS) (for details consult [13]).

2.3. Testing procedure

The density of the foamed nanocomposites was measured according to ISO-845. Foam morphology was analyzed using a JEOL JSM-5610 scanning electron microscope. Samples were prepared by brittle fracturing the foams using liquid nitrogen and sputter depositing a thin layer of gold onto the fractured surface.

The crystalline characteristics of the several polymers and GnP were analyzed by X-Ray diffraction (XRD) using a Panalytical diffractometer operating with CuKα radiation (λ = 0.154 nm) at 40 kV and 40 mA. Scans were taken from 2º to 60º using a scan step of 0.033º.

A DMA Q800 (TA Instruments) was used in a single cantilever configuration to study the influence of GnP and density on the storage modulus (*E'*) of the foams. Experiments were performed at 1 Hz at a heating rate of 2 °C/min applying a dynamic strain of 0.02%. Specimens were prepared with a nominal length of 35 mm, width of 13 mm and thickness of 3 mm.

The electrical conductivity of the foams was measured using a pA meter/dc voltage source HP model 4140B. Square-shaped samples about 2 cm × 2 cm in side and 0.5-1.0 mm thick were prepared from each foam and painted using colloidal silver conductive paint in order to guarantee a proper electrical contact between the electrodes and the sample's surface. A programmable dc voltage feature with a range of 0-20 V and a voltage step of 0.05 V, a hold time of 10 seconds and a step delay time of 5 seconds, was used.

3. Results and discussion

As foaming has been shown to add to a better dispersion of nanoparticles [7-9], the addition of GnP to polymers and later foaming could lead to the development of lightweight multifunctional materials, incorporating some of the already mentioned advantages of this conductive nanosized filler, such as improvement of the mechanical properties or enhancement of the electrical conductivity. Because only scarce works have considered the preparation of

polymer foams with graphene, there is still a considerable lack of information regarding the influence that GnP has on the microstructure and cellular structure and thus on the final properties of the resulting foams.

3.1. Improvement of the specific mechanical properties

As can be seen by the values of the specific storage modulus presented in Fig. 1(a) for PP foams containing 2.5 and 5 wt% GnP prepared by chemical foaming, the addition of increasingly higher amounts of GnP led to foams with improved specific mechanical properties, related to a combination of a more effective reinforcement effect of GnP resulting from a higher concentration and improved GnP dispersion throughout the PP due to foaming (see XRD spectra in Fig. 1(b) showing reduction (chemical foams) and in last case disappearance (physical foams) of GnP's (002) diffraction peak with reducing relative density), and the finer cellular structure (compare micrographs presented in Fig. 1(c)). Particularly, the specific elastic modulus of PP + 5% GnP foam was comparable to the value of the solid unfilled PP, demonstrating that for low GnP contents it was possible to obtain rigid PP foams with similar mechanical properties than those of the unfilled solid material but with important weight reductions [11].

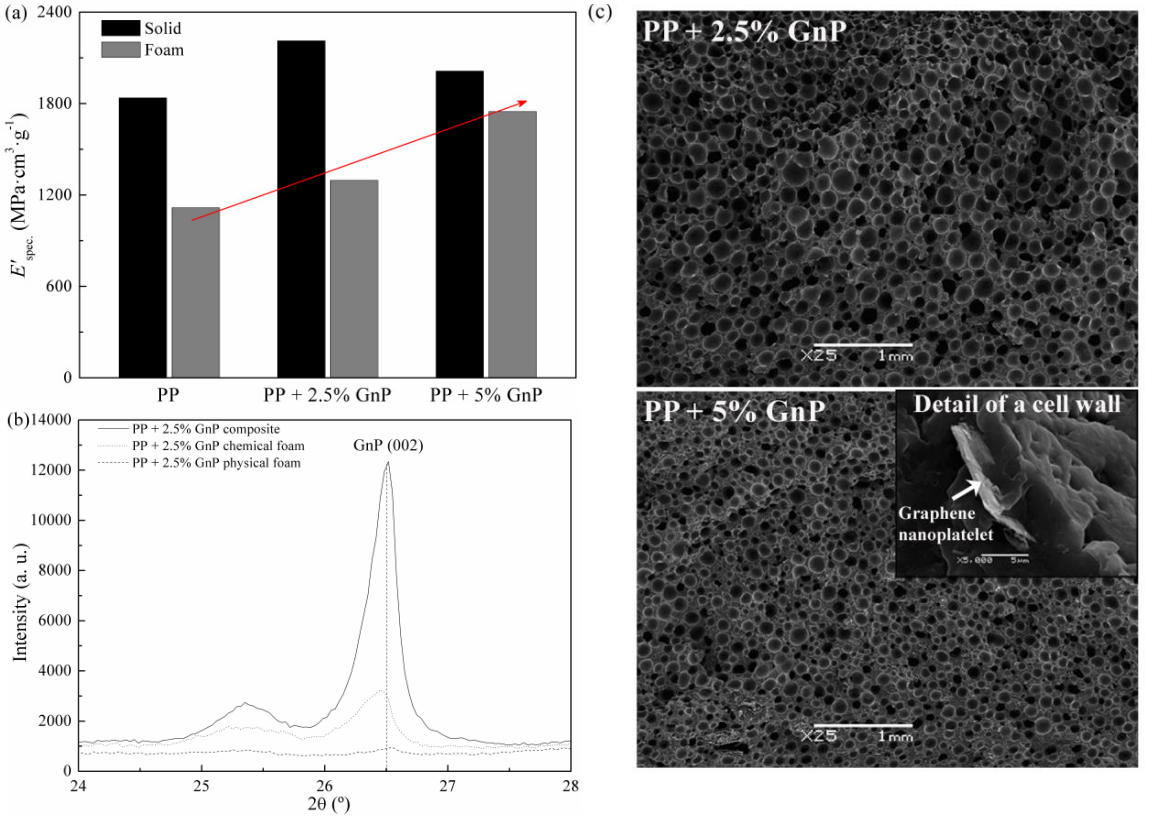

Fig. 1. (a) Specific storage modulus ($E'_{spec.}$) of unfilled and GnP-reinforced PP chemical foams; (b) XRD spectra of PP foams containing 2.5% GnP (physical foam: lower relative density) and (c) SEM micrographs of PP chemical foams containing 2.5 and 5% GnP.

Interestingly, the addition of even a small amount of GnP (0.5 wt%) to PC resulted in foams with enhanced storage moduli, as the combination of GnP and sCO_2 at the selected foaming conditions induced the partial crystallization of PC, restricting its molecular mobility and leading to stiffer foams [14].

In the same way as PP and PC foams with GnP, PEI foams reinforced with variable concentrations of GnP presented increasingly higher values of $E'_{spec.}$ with increasing the concentration of GnP (see Fig. 2(a)), once again

related to a higher stiffness of GnP. As expected, foams with higher relative densities presented higher values of the storage modulus, clearly exceeding that of the unfilled PEI foam (see Fig. 2(b)) [13].

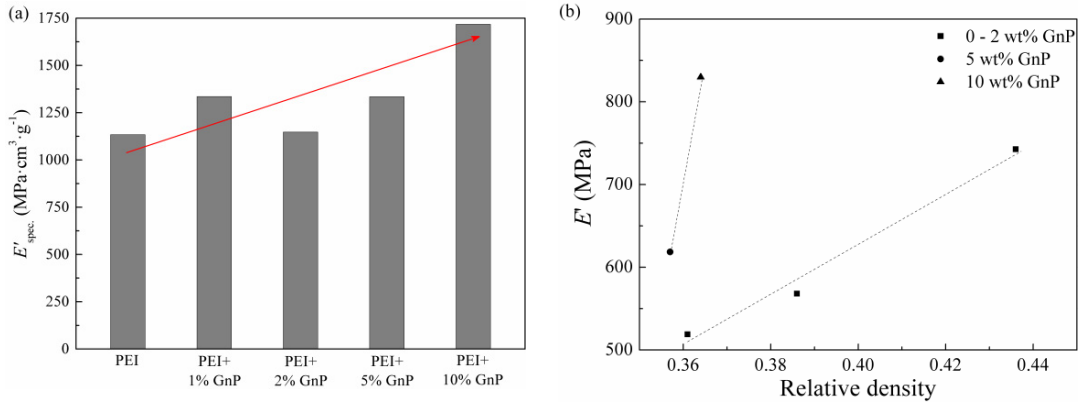

Fig. 2. (a) Evolution of $E'_{spec.}$ with GnP content and (b) evolution of E' with relative density for PEI foams containing GnP.

3.2. Enhancement of the electrical conductivity

Only recently the addition of graphene into polymer foams has been considered with the objective of enhancing their electrical conductivity, mainly for electrostatic discharge (ESD) or electromagnetic interference (EMI) shielding [15-19]. As shown in Fig. 3(a), the electrical conductivity of PC foams containing GnP increased with increasing the expansion ratio (ER), i.e., with reducing relative density, reaching a value > 10^{-6} S/m for an ER around 3. As GnP content was kept constant in these foams (0.5 wt%), it was possible to enhance their electrical conductivity with decreasing GnP's volume fraction, as lower densities lead to lower GnP volume contents. This is in apparent contradiction with the common behavior found for similar composites, where electrical conductivity has been shown to increase with reducing ER and increasing nanoparticle content. This electrical behavior proves that foamed nanocomposites are complex systems where electrical conduction is determined by the microstructure of the nanocomposite in the cell walls and struts. One of the important factors is the improved dispersion of nanoparticles with foaming, as proven in Fig. 3(b) by the disappearance of the peak corresponding to the (002) crystal plane of GnP, which, combined with a reduction of the available volume, leads to a significant reduction of the distance between nanoparticles and to enhanced electrical conductivities by mechanisms such as tunneling [20].

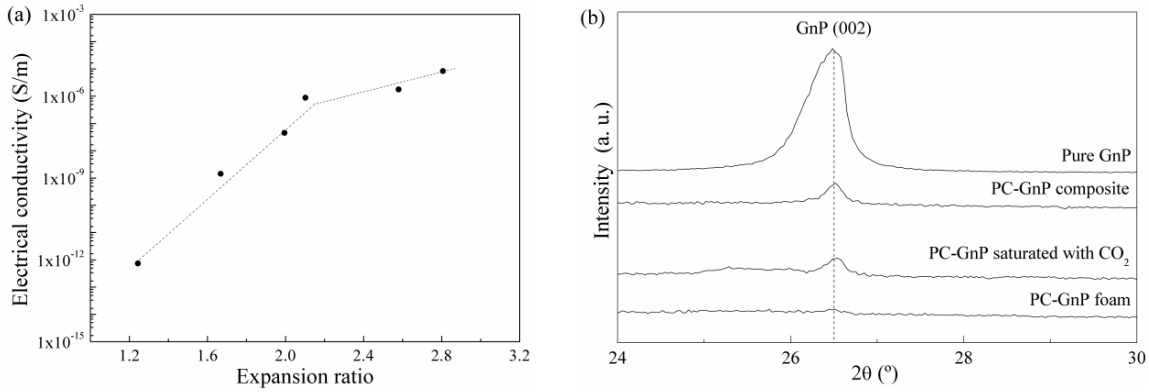

Fig. 3. (a) Evolution of the electrical conductivity with ER for PC-GnP foams and (b) XRD spectra showing GnP's (002) peak reduction with processing and disappearance with foaming.

PEI-GnP foams presented an increase in electrical conductivity from the 1.0×10^{-15} S/m of unfilled PEI up to 1.8×10^{-7} S/m at 10 wt% GnP (promising for ESD applications), indicating that a conductive network of GnP was formed throughout the cell walls and struts. As seen in Fig. 4(a), the electrical conductivity of PEI foams followed a linear-like increasing trend with augmenting the amount of GnP, indicating that the electrical conductivity of the foams was controlled by GnP's content. Although a conductive path was formed, once again the mechanism that best fitted the values and evolution of the electrical conductivity was that based on tunnel conduction, as no GnP percolation threshold was found and absolute values were clearly below what should be expected based on direct contact between nanoplatelets, in a similar way as other polymer foams containing carbon-based particles [9,21]. Fits assuming a tunnel mechanism led to the existence of a GnP network with a 3D random distribution, once again related to an improved dispersion of GnP stacks throughout the PEI matrix promoted by foaming (see scheme of improved electrical conduction due to reduction of the critical distance between GnP presented in Fig. 4(b)) [13].

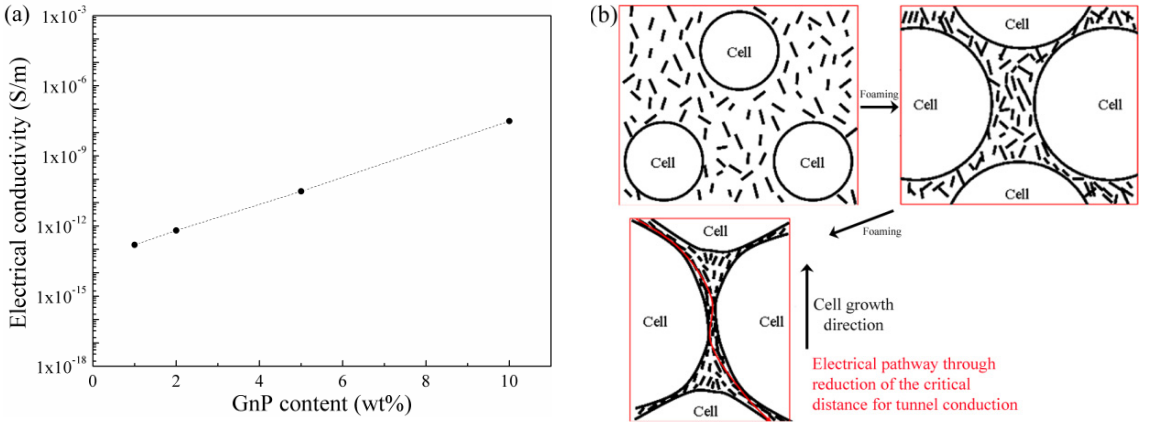

Fig. 4. (a) Evolution of the electrical conductivity with GnP content for PEI-GnP foams and (b) scheme of improved electrical conduction by tunnel mechanism due to reduction of the critical distance between GnP with foaming.

4. Conclusions

Owing to its properties and mass production scalability, GnP has found an increasing interest in the preparation of polymer nanocomposites. However, processing is still a challenge due to difficulties in dispersion. Foaming could come as a strategy, as it has been shown to favor the dispersion of nanoparticles throughout polymers.

The addition of GnP into polymers and foaming has been shown to result in foams with improved mechanical properties, as on the one hand foaming enhances GnP dispersion throughout the polymer, maximizing GnP's reinforcement effect, and, on the other, GnP induces the formation of finer cellular structures. In some specific cases, the combination of GnP and sCO_2 during foaming promotes polymer crystallization, leading to stiffer foams. These microstructure modifications enable to obtain foams with a mechanical performance clearly exceeding that of unfilled foams and in some cases even comparable to the unfilled solid material.

GnP addition into polymer foams may also lead to significant enhancements of their electrical conductivity, the final value being dependent upon the nanocomposite microstructure. As foaming promotes GnP dispersion and at the same time reduces the volume fraction of solid, there is a reduction of the distance between nanoplatelets, reaching the critical distance for tunnel-like electrical conduction. Foams may display electrical conductivities that are even higher than that of the respective unfoamed composites, which, in combination with optimized mechanical performance, opens up new uses for these materials as ESD, EMI shielding or piezoelectric rigid components.

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